Ultra-slow dynamics in low density amorphous ice revealed by deuteron NMR: indication of a glass transition

Florian Löw,*a Katrin Amann-Winkel,b Thomas Loerting,b Franz Fujaraa and Burkhard Geilc

The postulated glass–liquid transition of low density amorphous ice (LDA) is investigated with deuteron NMR stimulated echo experiments. Such experiments give access to ultra-slow reorientations of water molecules on time scales expected for structural relaxation of glass formers close to the glass–liquid transition temperature. An involved data analysis is necessary to account for signal contributions originating from a gradual crystallization to cubic ice. Even if some ambiguities remain, our findings support the view that pressure amorphized LDA ices are of glassy nature and undergo a glass–liquid transition before crystallization.

1 Introduction

In recent years it became more and more evident that thermal as well as dynamic properties of the disordered low temperature states of water strongly depend on the history of the sample and especially on the pathways taken in a pVT-diagram during the preparation of the phases. The original distinction between two (high- and low density) amorphous ices (HDA and LDA) introduced by Mishima et al.1 nowadays seems to be a rough classification scheme only, where we know many (re)producible variations within both classes. In the first place it is not the variability in physical properties itself that is surprising. All simple glass formers have inherited the physical properties of the liquid at the ‘fictitious temperature’ where the molecular kinetics of the liquid was ‘frozen in’ and thus their properties vary depending on the thermal sample history.

Most amorphous ices, however, do not directly stem from a frozen liquid state but are produced by a pressure-induced collapse of crystalline ice structures. Are they nevertheless related to a well-defined, higher temperature equilibrium liquid state?2–8 Or are they the crushed, disordered, and fully out-of-equilibrium remains of a crystal structure?9–13 If they are glasses, which of those many amorphous variations are the possibly frozen-in liquid states? Considering LDL and HDL as liquid analogs to LDA and HDA is obviously already established in the literature.14,15 But then, do we – maybe – have a broad spectrum of LDLs and HDLs? On the other hand, if they are ‘undefined’ remains of a microscopically destroyed crystal, do they relax into a structure that is equivalent to a liquid that really exists at higher temperatures? Obviously, all of them seem to relax into some well-defined predefined direction. The central question is whether or not there is experimental evidence of a glass–liquid transition prior to (or hidden by) the HDA-to-LDA or the LDA-to-ice Ic transition.

During the last decade it was realized that a certain member of the LDA class of amorphous ices, previously called ‘LDA-II’,† exhibits a significantly extended range of thermal stability.6,17 In LDA-II the onset of crystallization into cubic ice Ic is shifted by as much as 10 K up to higher temperatures when compared to other unrelaxed species of the LDA class. For LDA being a glass, a temperature interval of 10 K – close to the calorimetric Tg6,18 – would imply a tremendous gain in accessible time scales for the α-relaxation. Could the gain of these 10 K on

† Nelmes et al.16 demonstrated that the state of relaxation of high density amorphous ice affects its properties quite significantly and therefore emphasized the necessity to distinguish between the original1 unrelaxed or unannealed form of HDA (uHDA) and the one which is relaxed/annealed close to the transition to LDA (so called expanded HDA, eHDA). Recently, it became clear that the degree of relaxation of HDA influences the thermal stability and the intermediate range structural ordering of LDA forms, being called LDA-I (obtained from uHDA) and LDA-II (obtained from eHDA).6,17
the low temperature border of the so-called ‘no-man’s land’ in the phase diagram of amorphous ices yield the key to access the liquid side of the glass-liquid transition? If not, could we at least observe the glass typical divergence of structural relaxation times? Or, in the worst case, could we, maybe, see some indications of it?

This study is not the first attempt to enter the new 10 K extension of temperature range of the no man’s land’s border using the stability of LDA-II. In previous work, we analyzed the new candidates eHDA and its derivative LDA-II in terms of quasielastic neutron scattering and deuteron (2H) NMR spin-relaxation thereby looking for anomalies in the Debye–Waller factor and nuclear spin–lattice relaxation enhancement, respectively, which might then be attributed to fast glass-typical secondary processes. Our findings did not provide a clear-cut message pro or contra a glass–liquid transition.

Now, with this work, we will try to track the structural relaxation itself, utilizing 2H-NMR which is able to access the ultra-slow reorientation dynamics that has to be associated with any structure relaxation in all ice-like water-networks due to the Bernal– Fowler ice rules. 2H-NMR offers two complementary anchor points to study dynamic processes: spin–lattice relaxation is ‘easy’ to measure but ‘hard’ to interpret without ad hoc model assumptions while stimulated echoes are much ‘harder’ to measure but offer an ‘easy’ and, even more important, an unambiguous, model-free interpretation. We will use a combination of both techniques that has proven to be a powerful tool for investigations of the glass–liquid transition in many simple glass former model systems in the past.21,22

Fig. 1 shows the essential findings of those studies: above the caloric glass–liquid transition temperature $T_g$ of molecular glass formers one observes the so-called $\alpha$-process characterized by the structural relaxation time $\tau_\alpha$. The experimental spin–lattice relaxation times $T_1$ display a minimum at that temperature where the time constant of the relevant motional process equals the inverse Larmor frequency. As long as $T_1$ stems from the $\alpha$-process it should follow the temperature dependence of $T_{1,\alpha}$. From relaxation theory it is known that at temperatures below the $T_1$ minimum (the so-called slow motion regime) $T_{1,\alpha} = C\tau_\alpha$ with $C \approx 10^3 \ldots 10^5$ for typical 2H quadrupolar coupling constants and Larmor frequencies of around 40 to 50 MHz.23 Experimentally, however, close to $T_g$ the $T_1$ relaxation tends to be dominated by fast secondary processes. This results in a temperature dependence of $T_1$ being weaker than that of $T_{1,\alpha}$ such that close to $T_g$, $\tau_\alpha$ eventually crosses $T_1$. Below $T_g$ the $T_1$ relaxation behavior is determined by dynamic properties of the amorphous structure such as phonon-like excitations or librations with decreasing amplitudes as temperature is decreased.

2 Experimental

2.1 Deuteron NMR

The NMR experiments are performed at a $^3$H Larmor frequency of 46.7 MHz. Strong rf pulses (with $\pi/2$ pulse lengths of about 2.0 $\mu$s) have been applied to ensure full excitation of the broad deuteron powder spectra.

$^2$H-NMR is an excellent tool for observing O–$^2$H bond reorientations, since the orientation-dependent frequency shift $\omega_Q$ is dominated by the quadrupole interaction of the deuteron:

$$\omega_Q = \frac{\delta}{2} \left(3 \cos^2 \theta - 1 - \eta \sin^2 \theta \cos 2\phi\right)$$

where $\theta$ is the angle between the O–$^2$H bond and the external magnetic field, $\delta = \frac{1}{2} e^2 q Q / h$ is related to the quadrupole coupling constant $e^2 q Q / h = (218.6 \pm 1.0)$ kHz for O–$^2$H bonds in LDA-II.$^{24}$

Magnetization recovery curves $M(t)$ are measured by application of a saturation pulse sequence with variable waiting time. The obtained recovery curve is parameterized by a stretched-exponential function (Kohlrausch law):

$$M(t) = M_0 \left(1 - \exp \left[-\left(t / T_1\right)^{\beta}\right]\right).$$

with the time constant $T_1$ and the stretching parameter $\beta$.

Using the $^2$H stimulated echo experiment “($\pi/2$) – $\tau$ – ($\pi/2$) – $t_m$ = ($\pi/2$) – $\tau$ – echo” we can directly measure a single particle reorientation correlation function of a tagged O–$^2$H bond orientation relative to the external magnetic field direction and therefore obtain information about geometry and the time scale of the bond reorientational motion. The echo amplitude $S(\tau, t_m)$ correlates the quadrupole frequency of a tagged deuteron during the dephasing period of length $\tau$ with its quadrupole frequency during the rephasing period of length $t_m$ after mixing time $t_m$. For $\tau \ll t_m$ the amplitude is25–27

$$S(\tau, t_m) = S_0 \exp(-k_0(0)e^{-k_0(t_m)\tau}).$$

† The anisotropy parameter of the electric field gradient $\eta = 0.102 \pm 0.006$ (ref. 24) is negligible in our context.
The brackets ( ) denote the ensemble average. The experimental data are parameterized by a stretched-exponential decay towards a plateau value, i.e.,

\[ S(t, t_m) \propto (1 - S_\infty(t)) \exp\left[-\left(\frac{t_m}{\tau_c(t)}\right)^{\gamma(t)}\right] + S_\infty(t) \] (4)

The \( \tau \)-dependent parameters are the time constant \( \tau_c(t) \), the Kohlrausch parameter \( \gamma(t) \) and the long time plateau value \( S_\infty(t) \).

The amplitude of the stimulated echo experiment is not only reduced by correlation loss but also due to spin–lattice relaxation. This additional decay has to be considered as pointed out in ref. 28.

### 2.2 Sample preparation

The samples are prepared from \( ^2\text{H}_2\text{O} \) (99.9\% deuterated) purchased from eurisotop. The preparation technique is described in detail by Winkel et al.\(^{29}\) In short: LDA-II is obtained after isothermal compression of ice \( \text{I}_h \) at 110 K followed by heating to 160 K at a pressure of 1.1 GPa. Very high density amorphous ice (VHDA), obtained in this way, is subsequently decompressed isothermally at 143 K with a rate of 13 MPa min\(^{-1} \) to 8 MPa towards LDA-II. The decompression is followed by quenching to 77 K. The sample preparation has been identical to that in ref. 17, 19 and 20. X-ray powder diffractograms confirm the low density amorphous nature of all samples. Care has been taken not to exceed 85 K when transferring them into the flow cryostat of an NMR spectrometer. The temperature stability is estimated to be \( \pm 0.5 \) K over several days.

### 3 Results and discussion

In previous works, deuteron \( T_1 \) was established as a sensitive monitor parameter to verify the thermal limits of stability of various ice phases.\(^{20,30,31}\) One central outcome of all those experiments was the finding that most LDA species show a slow annealing towards a common state when the temperature is cycled inside the stability range of these phases. As far as one can conclude from NMR experiments alone, the common state could be identical with LDA-II – a hypothesis that is supported by the fact that LDA-II itself shows no annealing in the whole range of its extended thermal stability.

#### 3.1 Characterization of the sample states with \( T_1 \)

In the present work, stimulated echo experiments are used to obtain temperature dependent \( \tau \)-relaxation times of LDA-II. For each temperature point the stimulated echo experiment is embedded within two \( T_1 \) measurements. This time consuming procedure is necessary to verify the sample stability, a precondition for the data interpretation that follows.

Fig. 2 demonstrates the quality of data underlying these control experiments. Fig. 2a shows a magnetization recovery after a saturation pulse sequence together with two least-square fit results. The dashed line, which corresponds to the residue plot shown in Fig. 2b, is obtained by fitting the data with a simple mono-exponential recovery function. Systematic deviations much stronger than the scatter in the data lead to the conclusion that the \( T_1 \) decay is not mono-exponential. Using a stretched exponential fitting function instead (the solid line and the residue plot in Fig. 2c) results in a parameterization that is flexible enough to modulate the recovery curves.
Both fit parameters, $T_1$ as well as $\beta$, are suitable to monitor changes in the sample state. Their temperature dependence is shown in Fig. 2d and e for a complete LDA-II transition sequence ($\text{LDA-II} \rightarrow \text{I}_c \rightarrow \text{I}_c/\text{I}_h \rightarrow \text{I}_h$) finally ending in hexagonal ice.

In this sequence one can clearly discriminate between three domains: below $\approx 140$ K $T_1$ and $\beta$ are characteristic of LDA-II.[20] Above 144 K the relaxation parameters indicate that LDA-II has transformed to crystalline cubic ice $\text{I}_c$. It is noteworthy that over quite a wide temperature range between 144 K and $\approx 175$ K $T_1$ does not change but $\beta$ does. Between 180 K and 215 K the relaxation parameters gradually approach those found in hexagonal ice $\text{I}_h$. This substantiates the hypothesis of gradual formation of hexagonal ice in a cubic ice matrix.[32–35] Finally, above 215 K, $T_1$ and $\beta$ are in agreement with relaxation parameters of ice $\text{I}_h$.[36] However, these findings – highly interesting for the study of crystalline ice phases themselves – are beyond the scope of this paper.

### 3.2 Gradual crystallization

A second observation, most important for the study of the LDA-II phase, is the failure of the stretched-exponential fits starting at temperatures slightly below the LDA-II $\rightarrow \text{I}_c$ transition (Fig. 3a and the residue plot in Fig. 3b). Obviously, the magnetization recovery becomes bimodal and, indeed, fitting with a superposition of two stretched-exponentials

\[
M(t) = M_0\left(1 - M_{\text{LDA}}\exp\left[-\left(\frac{t}{T_{\text{LDA}}}\right)^{\beta_{\text{LDA}}}\right]\right) - M_0\exp\left[-\left(\frac{t}{T_{\text{I}}^c}\right)^{\beta_{\text{I}}^c}\right].
\]

The occurrence of bimodality is irreversible in the sense that when decreasing the temperature again, the LDA-II magnetization recovery curves stay bimodal. This suggests, without doubt, that the onset of crystallization contaminates the LDA-II phase with traces of ice $\text{I}_c$. These traces are frozen in and do not vanish when the temperature is lowered.

Fig. 4 is a test of this hypothesis. The bimodal fits provide the amplitudes, i.e., the relative amounts of both contributions. The fraction of cubic ice plotted versus the consecutive number of the measurement (Fig. 4a) and compared to the temperatures of the measurements (Fig. 4b) clearly demonstrates the growth of cubic crystallites at higher temperatures and their conservation at lower temperatures.[8] This gradually growing contamination with ice $\text{I}_c$ will be crucial for the analysis of the stimulated echo experiments. However, with the alternating sequence of $T_1$ and stimulated echo experiments we do have all the tools necessary for a precise correction of these effects.

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**Fig. 3** (a) Magnetization recovery curve at 137.5 K and the best bimodal stretched-exponential fit (black solid line) that is composed by one component associated to LDA-II (dotted line) and another to cubic ice (dashed line). The residue plots show the deviation $\Delta = M(t)_{\exp} - M(t)_{\text{fit}}$ between the experimental data and the fit for a stretched-exponential (b) and bimodal (c) parametrization.

**Fig. 4** (a) Chronology of temperature settings in subsequent experiments. (b) Relative amount of cubic ice $\text{I}_c$ as deduced from magnetization decay curves.

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§ This observation does not contradict statements of our previous publication[20] where we had measured $T_1$ by more rapid $T$ scans such that crystallization had usually not occurred before the next $T$ step.
3.3 Molecular reorientation dynamics

The central experiment of this investigation is the stimulated echo experiment which gives direct access to molecular reorientation times. All stimulated echo decay curves have been measured at a fixed evolution time τ = 7 μs (mid-pulse to mid-pulse). A typical decay of the stimulated echo amplitude is presented in Fig. 5. Obviously, the stimulated echo decay is not much faster than the T₁ relaxation, and both time scales have to be separated by a procedure as indicated at the end of Section 2.1. That is, the experimental data are divided by the interpolated magnetization loss obtained from the independent T₁ measurements. Therefore the remaining decay is given by molecular reorientation exclusively. A fit with eqn (4) now yields three parameters, the final state, S∞, the correlation time, τc, and the stretching parameter, β. γ is found to be essentially temperature independent, its value of 0.72 ± 0.07 is similar to the values expected from other molecular glass formers.

At this point we are faced with the crucial question: is the stimulated echo decay connected with the glass–liquid transition θ-process? This would be the case if the stimulated echo decay time tₑ can be identified with the structural relaxation time τc.

Several prerequisites have to be fulfilled in order to substantiate this conjecture.

(i) The final state of the stimulated echo decay must be non-zero if the stimulated echo decay originates from molecular reorientation. Its values are unequivocally determined by the geometry of reorientation, e.g., S∞(7 μs) ≈ 0.25 for tetrahedral jumps (as found in crystalline ice Ih⁰), or S∞(7 μs) ≈ 0.1 for fully isotropic reorientation (which one could expect in glasses).

(ii) As indicated in Fig. 1, in the vicinity of Tg the θ-process time scale crosses the T₁ curve. Thus, the stimulated echo decay time tₑ(T) must necessarily decouple from T₁(T).

(iii) At Tg τg should be in the order of 100 seconds and τc must not be too far away from this value. Furthermore, the temperature dependence of τc must result in a “reasonable” glass typical activation energy.

Let us start with item (i), by inspecting the final states. In Fig. 6 S∞(τ = 7 μs) is plotted as a function of temperature. The figure clearly shows that at temperatures above ≈ 135 K S∞ is non-zero. However, due to the large scatter of the data (data of several samples are included) one cannot decide between the two reorientation scenarios mentioned above. In other words with S∞ one cannot distinguish between crystal- and glass-like dynamics. The scatter as well as the temperature dependence in the S∞ data originate from the data analysis procedure, see below. The vanishing separation in the time scales of τg and T₁ at lower temperatures prevents a stable determination of S∞. The data become more reliable at higher temperatures.

Fig. 7 deals with item (ii), the separation of time scales. A small but highly significant decoupling between τc and T₁ with increasing temperature is obvious. But here again, the lacking time scale separation prevents a trustworthy analysis of the correlation times below ≈ 135 K. The ratio between τg and T₁ plotted in Fig. 7b decreases to values down to 0.1 – a clear indication that T₁ even at the highest temperatures before crystallization is not T₁,θ, cf. Fig. 1.

Item (iii) can be discussed in the context of Fig. 8 which shows an Arrhenius plot of the reorientational correlation times, τc. Due to the merging of the T₁ and τg-time scales at lower temperatures, this plot is now restricted to the temperature range above 133 K. Again, this plot contains data from several samples indicated by different symbols. An Arrhenius type T-dependence, i.e., τc ∝ exp(Ea/kT), with Ea = (22.4 ± 2) kJ mol⁻¹ is obtained in this temperature range. The activation energy is of the order of the bond strength of hydrogen bonds; it corresponds to values observed in the Bjerrum defect dynamics in crystalline ice Ih⁰.

If we adopt the technical definition of a glass–liquid transition temperature being that temperature where τc becomes 100 seconds, we can extrapolate the straight line in Fig. 8 to see that τc arrives at this value at T = 126 K. This value, located deep in the stability range of LDA-II, is significantly smaller than Tg = 145 K obtained by calorimetric measurements with a heating rate of 10 K min⁻¹ on both LDA-I and LDA-II ices. But it is very close to the Tg of 124 K obtained by

![Fig. 5 Typical decay curve of the stimulated echo amplitude in LDA-II: the sampled data (open triangles) has been divided by the effective magnetization M*(t_m) (dashed line) to obtain the stimulated echo decay (full diamonds) which is then fitted by eqn (4) (solid line).](image-url)

![Fig. 6 Final states S∞(τ = 7 μs) as a function of temperature for various samples (indicated by different symbols).](image-url)
Handa and Klug for LDA-I samples at a heating rate of 10 K h$^{-1}$ using Tian–Calvet calorimetry. 18

4 Conclusions

The presented stimulated echo experiments unravel the presence of an ultra-slow reorientation dynamics in LDA-II in the vicinity of the postulated glass–liquid transition temperature. We find time scales in the order of several ten seconds which are of the order of those expected for glass forming liquids. Is this reorientation dynamics the $\alpha$-relaxation of a supercooled liquid? Or in short, is $\tau_c = \tau_\alpha$? For this, we have formulated three criteria which have to be fullfilled.

Essentially, all our experimental results seem to support the view that $\tau_c$ can be identified with $\tau_\alpha$. Our dynamic process takes place on a reasonable time scale, has a rational activation energy and the final states of the correlations function are finite. Furthermore, the short $T_1$ relaxation times agree with those found in other glasses and differ from the huge values found in crystalline ice phases. In this picture, LDA-II can be imagined as a gradually softening glass.

But do our findings really exclude other, maybe nano-crystalline scenarios? At this point we have to concede that they do not. Even if our final states are finite, they do not rule out a crystalline tetrahedral reorientation. This is because this experiment principally cannot answer the question whether the observed reorientational motion is accompanied or not by translational motion (diffusion) as expected in an ultraviscous liquid. Also, the measured activation energy, compatible with hydrogen bond breaking, is identical to that found in crystalline ices.

In summary, the outcome of these investigations provides strong but not unambiguous arguments supporting the view that LDA-II is a homogeneous glassy state of water.

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